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(54) Title: PROCESS FOR DELIGNIFICATION OF LIGNOCELLULOSE-CONTAINING PULP

(57) Abstract

The present invention relates to a process for delignifying and bleaching lignocellulose-containing pulp, in which the pulp is delignified with a peracid or a salt thereof, treated with a complexing agent, and subsequently bleached with a chlorine-free bleaching agent. Suitably, delignification is carried out with the strongly oxidising peracetic acid, giving a considerable increase in brightness and a considerable reduction of the kappa number after bleaching with a chlorine-free bleaching agent comprising at least one of a peroxide-containing compound, ozone or sodium dithionite, or optional sequences or mixtures thereof. The brightness-increasing effect is highly selective, i.e. the viscosity of the pulp is maintained to a comparatively great extent. Both the delignification and the treatment with a complexing agent are advantageously carried out at a close to neutral pH, thus minimising the need of pH adjustment and making it possible to use spent bleach liquor internally, e.g. for washing the pulp. By final bleaching with ozone and hydrogen peroxide, it is possible with the inventive process to produce softwood pulps having a brightness exceeding 90 % ISO, and to remove practically all lignin in the pulp while maintaining sufficient pulp strength.

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Process for delignification of lignocellulose-containing pulp

The present invention relates to a process for delignifying and bleaching lignocellulose-containing pulp, in which the pulp is delignified with a peracid or a salt thereof, treated with a complexing agent, and subsequently bleached with a chlorine-free bleaching agent. Suitably, delignification is carried out with the strongly oxidising peracetic acid, giving a considerable increase in brightness and a considerable reduction of the kappa number after bleaching with a chlorine-free bleaching agent comprising at least one of a peroxide-containing compound, ozone or sodium dithionite, or optional sequences or mixtures thereof. The brightness-increasing effect is highly selective, i.e. the viscosity of the pulp is maintained to a comparatively great extent.

Background of the Invention

Chlorine-free bleaching agents have long been used for bleaching mechanical pulps. In recent years, it has become increasingly common to bleach also chemical pulps with chlorine-free bleaching agents, such as hydrogen peroxide and ozone, even in the first stages. It has been considered necessary to pretreat the pulp directly after digestion and an optional oxygen-delignifying stage so as to avoid deteriorated pulp properties and an excessive consumption of the bleaching agent. Pretreatment of the pulp primarily involves acid treatment and treatment with a complexing agent or salts of alkaline-earth metals, optionally in combination. Strongly acid pretreatment removes desirable as well as undesirable metal ions from the original positions in the pulp. Treatment with suitable complexing agents primarily removes the undesirable metal ions, while the desirable ones are largely retained. Treatment with salts of alkaline-earth metals maintains or reintroduces the desirable metal ions.

EP-A-0 402 335 thus discloses the pretreatment of chemical pulp with a complexing agent directly after digestion or oxygen delignification, to make a subsequent alkaline peroxide bleaching more efficient.

EP-A-0 480 469 relates to delignification of lignocellulose-containing pulp with oxygen. The pulp can be delignified or bleached before or after the oxygen stage with peroxide-

containing compounds, such as hydrogen peroxide or peracetic acid, chlorine dioxide and/or ozone. Use of sequences with both peracetic acid and hydrogen peroxide, results in a significant decrease in pulp viscosity.

With increasingly stringent environmental standards, there is a growing need for completely chlorine-free processes for delignifying and bleaching lignocellulose-containing pulps. To produce fully bleached pulps with unaltered strength properties in a reasonable number of stages and with a reasonable consumption of bleaching agents, it has become necessary to consider using also powerful, and hence difficultly-controlled, bleaching agents having a high delignifying and/or bleaching capacity.

Description of the Invention

The invention provides a process in which lignocellulose-containing pulp is delignified and bleached under the conditions disclosed in the appended claims, whereby a good delignifying and bleaching effect is obtained even before the chlorine-free bleaching.

The inventive process comprises delignifying and bleaching lignocellulose-containing pulp, wherein the pulp is delignified with a peracid or salts thereof, whereupon the pulp is treated with a complexing agent and subsequently bleached with a chlorine-free bleaching agent comprising at least one of a peroxide-containing compound, ozone or sodium dithionite, or optional sequences or mixtures thereof.

The inventive process has made it possible to delignify the pulp before a chlorine-free bleaching, such that the subsequent treatment with a complexing agent can be used for optimising the conditions for the subsequent chlorine-free bleaching, taking into consideration the desirable and undesirable metal ions. Thus, ions of alkaline-earth metals, especially when in their original positions in the pulp, are known to have a favourable effect on the selectivity in bleaching and the consumption of chlorine-free bleaching agents, such as peroxide-containing compounds and ozone.

In the invention, peracid or salts thereof include organic and inorganic peracids or salts thereof. As organic peracid, use is made of aliphatic peracids, aromatic peracids

or salts thereof. Suitably, peracetic acid or performic acid is used. As inorganic peracid, use is suitably made of peroxomonosulphuric acid (Caro's acid) or salts of inorganic peracids, such as peroxocarbonate, various perborates or peroxosulphates. Sodium is suitably used as cation in the salts, since such salts normally are inexpensive and sodium occurs naturally in the chemical balance in the pulp mill. Preferably, peracetic acid, peroxomonosulphuric acid or a salt thereof is used. Peracetic acid is especially preferred, being advantageous in terms of production and use. In addition, peracetic acid has limited corrosiveness. Any wastewater containing, inter alia, the degradation products of peracetic acid can be easily used for washing or recycled to the chemical recovery system.

According to the inventive process, peracetic acid can be produced by reacting acetic acid and hydrogen peroxide, giving what is known as equilibrium peracetic acid, by distilling equilibrium peracetic acid to remove hydrogen peroxide, acetic acid and sulphuric acid, or by reacting acetic acid anhydride and hydrogen peroxide directly in the bleaching stage, giving what is known as in situ peracetic acid. A typical equilibrium peracetic acid contains about 42% of peracetic acid and about 6% of hydrogen peroxide, i.e. the weight ratio of peracetic acid to hydrogen peroxide is here about 7:1. When equilibrium peracetic acid is used in the present process, the weight ratio between peracetic acid and hydrogen peroxide can be in the range of from about 10:1 to about 1:60, suitably from 7:1 to 1:15 and preferably from 2.8:1 to 1:2.

The added amount of peracid or salts thereof should be in the range of from about 1 kg up to about 100 kg per tonne of dry pulp, calculated as 100% peracid or salt thereof. Suitably, this amount lies in the range of from 2 kg up to 45 kg per tonne of dry pulp, and preferably in the range of from 3 kg up to 25 kg per tonne of dry pulp, calculated as 100% peracid or salt thereof.

Suitably, delignification with peracid or salts thereof is carried out at a pH in the range of from about 2.5 up to about 12. In preferred embodiments, where delignification is

carried out with peracetic acid or peroxomonosulphuric acid, the pH lies suitably in the range of from 3 up to 10, and preferably in the range of from 5 up to 7.5. Delignification with the other peracids or salts thereof mentioned above takes place within the normal pH ranges for the respective bleaching agents, these being well-known to those skilled in the art.

In the pulp, manganese ions, inter alia, have a particularly adverse effect on the bleaching with chlorine-free bleaching agents, such as ozone and alkaline peroxide compounds. Thus, compounds forming strong complexes with various manganese ions are primarily used as complexing agents. Such suitable complexing agents are nitrogenous organic compounds, primarily nitrogenous polycarboxylic acids, nitrogenous polyphosphonic acids and nitrogenous polyalcohols. Preferred nitrogenous polycarboxylic acids are diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), DTPA and EDTA being especially preferred. Diethylenetriaminepentaphosphonic acid is the preferred nitrogenous polyphosphonic acid. Also other compounds can be used as complexing agents, such as polycarboxylic acids, suitably oxalic acid, citric acid or tartaric acid, or phosphonic acids. Other usable complexing agents are such organic acids as are formed during the pulp treatment with, inter alia, chlorine-free bleaching agents.

The pH in the treatment with a complexing agent is of decisive importance in removing the undesirable trace metal ions while at the same time retaining the desirable ions of alkaline-earth metals. A suitable pH range depends, inter alia, on the type and the amount of trace metal ions in the incoming pulp. In the inventive process, the treatment with a complexing agent should be carried out at a pH in the range of from about 2.5 up to about 11, suitably in the range of from 3.5 up to 10, and preferably from 4.5 up to 9.

The selection of temperature in the treatment with a complexing agent is of major importance for removal of the undesirable trace metal ions. Thus, the content of manganese ions decreases with increasing temperature in the treatment with a complexing agent, which gives an increase in brightness and a reduction of the kappa number. For instance, when inc-

reasing the temperature from 20°C to 90°C, there is also, surprisingly, a noticeable increase in viscosity. The treatment with a complexing agent should be carried out at a temperature of from 26°C up to about 120°C, suitably from 26°C up to about 100°C, preferably from 40°C up to 95°C, and most preferably from 55°C up to 90°C.

The added amount of complexing agent depends on the type and the amount of trace metal ions in the incoming pulp. This amount is also affected by the type of complexing agent as well as the conditions in the treatment with a complexing agent, such as temperature, residence time and pH. The added amount of complexing agent should, however, be in the range of from about 0.1 kg up to about 10 kg per tonne of dry pulp, calculated as 100% complexing agent. Suitably, the amount lies in the range of from 0.3 kg up to 5 kg per tonne of dry pulp, and preferably in the range of from 0.5 kg up to 1.8 kg per tonne of dry pulp, calculated as 100% complexing agent.

In preferred embodiments, where both the delignification with peracid and the treatment with a complexing agent are carried out at a close to neutral pH, the need of pH adjustment is minimised. As a result, also the spent liquors from the bleaching and treatment stages can be used internally for washing. This gives a small total wastewater volume, enabling a considerably more closed system in the pulp mill.

Chlorine-free bleaching agent comprises a peroxide-containing compound or ozone in an optional sequence or mixture. Sodium dithionite can also be used as chlorine-free bleaching agent. The peroxide-containing compound suitably consists of inorganic peroxide compounds, such as hydrogen peroxide or peroxomonosulphuric acid (Caro's acid). Preferably, the peroxide-containing compound is hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.

Using hydrogen peroxide as chlorine-free bleaching agent, the pulp can be treated at a pH of from about 7 up to about 13, suitably at a pH of from 8 up to 12, and preferably at a pH of from 9.5 up to 11.5. Bleaching with the other chlorine-free bleaching agents mentioned above takes place within the normal pH ranges for the respective bleaching agents, these being well-known to those skilled in the art.

The process according to the invention is suitably carried out with a washing stage after the treatment with a complexing agent. Washing efficiently removes the complexed trace metal ions that have an adverse effect on the following chlorine-free bleaching, primarily manganese ions but also ions of e.g. copper and iron. To retain in the pulp the alkaline-earth metal ions that are advantageous to the following chlorine-free bleaching, primarily magnesium and calcium ions, the pH should be at least about 4 in the washing stage. Suitably, the pH in the washing stage lies in the range of from 5 up to about 11, preferably in the range of from 6 up to 10.

The washing liquid may be fresh water, optionally with an addition of a pH-adjusting chemical, or wastewater from one or more bleaching stages or extraction stages, in such a way that a suitable pH in the washing stage is obtained. The washing liquid may also consist of other types of optionally purified wastewater, provided it has a low content of undesirable metal ions, such as manganese, iron and copper.

The term washing after the complexing agent treatment relates to methods for displacing, more or less completely, the spent liquid in the pulp suspension to reduce its content of, inter alia, dissolved trace metal ions in said suspension. The washing methods may entail an increase in the pulp concentration, for example by sucking-off or pressing. The washing methods may also entail a reduction of the pulp concentration, for example by dilution with washing liquid. Washing also means combinations and sequences where the pulp concentration is alternately increased and reduced, one or more times. In the present process, a washing method is chosen which, in addition to removing dissolved organic substance, also removes the trace metal ions released in the treatment with a complexing agent, while considering what is suitable in terms of process technique and economy.

Washing efficiency may be given as the amount of liquid phase displaced as compared with the liquid phase present in the pulp suspension before washing. The total washing efficiency is calculated as the sum of the efficiency in each washing stage. Thus, dewatering of the pulp suspension after a treatment stage from, say, 10% to 25% pulp concentration

gives a washing efficiency of 66.7%. After a subsequent washing stage in which the pulp is first diluted to 3% and then dewatered to 25%, a total washing efficiency of 96.9% is achieved with respect to soluble impurities. In the present process, the washing efficiency should be at least about 75%, suitably in the range of from 90% up to 100%, and preferably in the range of from 92% up to 100%. A washing efficiency in the range of from 96% up to 100% is especially preferred.

By using the inventive process, the conditions for the chlorine-free bleaching, are optimised such that a high brightness, kappa number reduction and viscosity are achieved with a minimum consumption of chlorine-free bleaching agent. This becomes possible without using any auxiliary chemicals, such as stabilisers and protective agents, in the chlorine-free bleaching. The remaining bleaching chemicals, such as hydrogen peroxide and alkali, may advantageously be used directly in the bleaching stage, the peracid stage or any other suitable stage, such that an optimum combination of process technique and production economy is obtained.

The term lignocellulose-containing pulp refers to pulps containing fibres that have been separated by chemical or mechanical treatment, or recycled fibres. The fibres may be of hardwood or softwood. The term chemical pulp relates to pulps digested according to the sulphate, sulphite, soda or organosolv process. The term mechanical pulp refers to pulp produced by refining chips in a disc refiner (refiner mechanical pulp) or by grinding logs in a grinder (groundwood pulp). The term lignocellulose-containing pulp also relates to pulps produced by modifications or combinations of the above-mentioned methods or processes. Examples of such pulps are thermomechanical, chemimechanical and chemi-thermomechanical pulps. Suitably, the lignocellulose-containing pulp consists of chemically digested pulp, preferably sulphate pulp. A lignocellulose-containing pulp consisting of sulphate pulp of softwood is especially preferred.

The process according to the invention can be applied to pulps with a yield of up to about 90%, suitably in the range of from 30% up to 80%, and preferably in the range of from 45% up to 65%.

The inventive process can be carried out in an optional position in the bleaching sequence, e.g. immediately after the making of the pulp. When the inventive process is applied to chemically digested pulp, this is preferably delignified in an oxygen stage before the delignification with peracid.

The inventive process can be applied to chemically digested pulps having an initial kappa number in the range of from about 2 up to about 100, suitably from 5 up to 60, and preferably from 10 up to 40. The kappa number is then measured according to the SCAN-C 1:77 Standard Method.

In the inventive process, the delignification with peracid should be carried out at a temperature in the range of from about 10°C up to about 140°C, suitably from about 10°C up to about 120°C, and preferably from about 10°C up to about 100°C. More preferably the delignification with peracid is carried out at a temperature in the range of from 30°C up to 90°C, and most preferably from 50°C up to 80°C. Delignification with peracid should be carried out for a period of time of from about 1 min up to about 960 min, suitably from 10 min up to 270 min, and preferably from 30 min up to 150 min. The pulp concentration in the delignification with peracid may be from about 1% by weight up to about 70% by weight, suitably from 3% by weight up to 50% by weight, preferably from 8% by weight up to 35% by weight and most preferably from 10% by weight up to 30% by weight.

In the inventive process, the treatment with a complexing agent should be carried out for a period of time of from about 1 min up to about 960 min, suitably from 15 min up to 240 min, and preferably from 35 min up to 120 min. In the treatment with a complexing agent, the pulp concentration may be from about 1% by weight up to about 60% by weight, suitably from 2.5% by weight up to 40% by weight, preferably from 3.5% by weight up to 25% by weight and most preferably from 5.5% by weight up to 25% by weight.

When using hydrogen peroxide as chlorine-free bleaching agent, the pulp should be treated at a temperature of from about 30°C up to about 140°C, and suitably from about 30°C up to about 120°C. Preferably the pulp is treated at a temperature of from about 30°C up to about 100°C and more preferably

from 60°C up to 90°C. The pulp should be treated for a period of time of from about 5 min up to about 960 min, suitably from 60 min up to 420 min, preferably from 190 min up to 360 min. When using hydrogen peroxide as chlorine-free bleaching agent, the pulp concentration may be from about 1% by weight up to about 70% by weight, suitably from 3% by weight up to 50% by weight, preferably from 8% by weight up to 35% by weight and most preferably from 10% by weight up to 30% by weight. Treatment with the other chlorine-free bleaching agents mentioned above takes place within the normal ranges as to temperature, time and pulp concentration for the respective bleaching agents, these being well-known to those skilled in the art.

In preferred embodiments using hydrogen peroxide as chlorine-free bleaching agent, the amount of hydrogen peroxide added in the bleaching stage should be in the range of from about 1 kg up to about 60 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide. The upper limit is not critical, but has been set for reasons of economy. Suitably, the amount of hydrogen peroxide is in the range of from 6 kg up to 50 kg per tonne of dry pulp, and preferably from 13 kg up to 40 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide.

In preferred embodiments using ozone as chlorine-free bleaching agent, the amount of ozone may be in the range of from about 0.5 kg up to about 30 kg per tonne of dry pulp, suitably in the range of from 1 kg up to 15 kg per tonne of dry pulp, preferably from 1.5 kg up to 10 kg per tonne of dry pulp and most preferably from 1.5 kg up to 5 kg per tonne of dry pulp.

After delignification with peracid, treatment with a complexing agent and subsequent chlorine-free bleaching, the pulp can be used for direct production of paper. The pulp may also be finally bleached to a desired higher brightness in one or more stages. Suitably, final bleaching is also carried out by means of such chlorine-free bleaching agents as are indicated above, optionally with intermediate extraction stages which can be reinforced by peroxide and/or oxygen. In this way, the formation and discharge of AOX is completely eliminated. It is also possible to use chlorine-containing bleaching agents, such as chlorine dioxide, in the final bleaching and

yet obtain a very limited formation and discharge of AOX, since the lignin content of the pulp has been considerably reduced by the present process.

The invention and its advantages will be illustrated in more detail by the Examples below which however, are only intended to illustrate the invention without limiting the same. The percentages and parts stated in the description, claims and Examples, refer to percent by weight and parts by weight, respectively, unless otherwise stated. Furthermore, the pH values given in the description, claims and Examples refer to the pH at the end of each treatment, unless otherwise stated.

In the Examples below, the kappa number, viscosity and brightness of the pulp were determined according to the SCAN Standard Methods C 1:77 R, C 15-16:62 and C 11-75:R, respectively. The consumption of hydrogen peroxide and peracetic acid were established by titration with sodium thiosulphate, and potassium permanganate and sodium thiosulphate, respectively.

<u>Example 1</u>

Oxygen-delignified sulphate pulp of softwood having a kappa number of 12.4, a brightness of 38.4% ISO, and a viscosity of 1100 dm^3/kg was delignified with peracetic acid (PAA), treated with EDTA and bleached with hydrogen peroxide, to illustrate the effect of pH in the treatment with a complexing agent. The added amount of peracetic acid was 22.4 kg/tonne dry pulp, calculated as 100% peracetic acid. In the delignification, the temperature was 70°C, the treatment time 60 min, the pulp concentration 10% by weight, and the pH 5-5.5. After delignification, the pulp was treated with 2 kg EDTA/tonne dry pulp at varying pH, a temperature of 90°C, a residence time of 60 min, and a pulp concentration of 10% by weight. The pulp was then bleached with hydrogen peroxide at a temperature of 90°C, a residence time of 240 min, and a pulp concentration of 10% by weight. The addition of hydrogen peroxide was 25 kg/tonne dry pulp, calculated as 100% hydrogen peroxide, and the pH was 10.5-11. After each stage, the pulp was washed with deionised water at a pH of 6.0. At this, the pulp was first dewatered to 25% pulp concentration and subsequently diluted to a pulp concentration of 3% by weight. After a few minutes, the pulp was dewatered to a pulp concentration of 25% by

weight. Thus, the total washing efficiency was about 97%. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE I

pH in the treatment with a complexing agent	Pulp properties after the H_2O_2 bleaching		
	Kappa number	Viscosity (dm³/kg)	Brightness (% ISO)
1.5	4.2	900	71
2.7	3.4	920	76
4.8	3.0	940	81
5.4	2.9	945	83
7.9	3.0	940	81
10.5	4.0	890	75
12.3	4.5	840	65

As is evident from the Table, treatment of pulp with a complexing agent according to the present invention results in a considerable increase in brightness and a considerable reduction of the kappa number reduction.

Example 2

Oxygen-delignified sulphate pulp of hardwood having a kappa number of 12.4, a brightness of 49.8% ISO, and a viscosity of 1270 dm³/kg was delignified with peracetic acid, treated with EDTA and bleached with hydrogen peroxide, to illustrate the importance of the complexing agent, and more specifically the importance of a treatment with a complexing agent in a separate stage. The conditions in the delignification with peracetic acid and the bleaching with hydrogen peroxide were as in Example 1. The conditions in the treatment with EDTA were as in Example 1, except that the pH was 5.8 throughout. For comparison, the pulp was treated in the absence of a complexing agent at a pH of 6.0, a temperature of 90°C and a residence time of 60 min (test 2). For further comparison, the pulp was delignified with peracetic acid in the presence of EDTA at a pH of 5.1, followed by bleaching with hydrogen peroxide (test 3). After each stage, the pulp was washed in accordance with Example 1. The results after the bleaching with hydrogen peroxide appear from the Table below.

TABLE II

Test	Pulp properties after the H_2O_2 bleaching Kappa number	Viscosity (dm³/kg)	Brightness (% ISO)
1	3.8	1063	87.2
2	4.7	1013	77.3
3	6.6	931	80.6

It is evident from the Table that treatment of pulp according to the present invention with a complexing agent in a separate stage results in a considerable increase in brightness and a considerable reduction of the kappa number while at the same time the highest viscosity of the pulp is achieved.

Example 3

The oxygen-delignified sulphate pulp of softwood used in Example 2 was treated according to the present process, to illustrate the effect of the initial delignification with peracetic acid on the pulp properties. The conditions in the delignification with peracetic acid, the treatment with EDTA, as well as the bleaching with hydrogen peroxide, were as in Example 2. For comparison, the pulp was treated with EDTA and bleached with hydrogen peroxide without any preceding delignification with peracetic acid (test 2). After each stage, the pulp was washed in accordance with Example 1. The results after the bleaching with hydrogen peroxide appear from the Table below.

TABLE III

Test	Pulp properties after the H_2O_2 bleaching Kappa number	Viscosity (dm³/kg)	Brightness (% ISO)
1	3.8	1063	87.2
2	7.5	1109	82.5

It is evident from the Table that delignification with peracetic acid before treatment with a complexing agent and bleaching with hydrogen peroxide yields a pulp having considerably higher brightness and lower lignin content while at the same time the difference in pulp viscosity is comparatively small.

Example 4

The oxygen-delignified sulphate pulp of softwood used in Example 1 was treated in accordance with the invention, followed by bleaching with ozone and hydrogen peroxide. The sequence used was peracetic acid - treatment with a complexing agent - hydrogen peroxide - ozone - hydrogen peroxide, i.e. PAA - Q - P - Z - P. The conditions in the delignification with peracetic acid, the treatment with EDTA, as well as the bleaching with hydrogen peroxide were as in Example 2. For comparison, the pulp was treated without delignification with peracetic acid, i.e. Q - P - Z - P (test 2). In the ozone stage, the pulp was bleached at a temperature of 25°C, a contact time of 2 min, and a pulp concentration of 37% by weight. The consumption of ozone was 2.6 kg/tonne dry pulp, and the pH was 2.1. In the second hydrogen peroxide stage, the pulp was bleached at a temperature of 70°C, a residence time of 60 min, and a pulp concentration of 10% by weight. The addition of hydrogen peroxide was 5 kg/tonne dry pulp, calculated as 100% hydrogen peroxide, the pH being 11.0. After each stage, the pulp was washed in accordance with Example 1. The results after the second hydrogen peroxide stage appear from the Table below.

TABLE IV

	Pulp properties after the H_2O_2 bleaching		
Test	Kappa number	Viscosity (dm^3/kg)	Brightness (% ISO)
1	0.4	750	90.3
2	0.9	800	86.9

It is evident from the Table that treatment of pulp according to the present invention, followed by bleaching with ozone and hydrogen peroxide, allows completely chlorine-free bleaching to above 90% ISO as well as removal of practically all lignin in the pulp while maintaining sufficient pulp strength.

Example 5

Oxygen-delignified sulphate pulp of softwood having a kappa number of 16, a brightness of 37.1% ISO and a viscosity of 1010 dm^3/kg, was treated in accordance with the invention

with two kinds of equilibrium peracetic acid and with a varying amount of peracetic acid (PAA), in order to illustrate the effect of hydrogen peroxide in the peracetic acid used. The conditions in the delignification with peracetic acid, treatment with EDTA as well as the bleaching with hydrogen peroxide were as in Example 2. In one of the equilibrium peracetic acids (PAA-1), the weight ratio between peracetic acid and hydrogen peroxide was 2.1:1. In the other equilibrium peracetic acid (PAA-2), the weight ratio between peracetic acid and hydrogen peroxide was 9.1:1. The same amount of peracetic acid was added when using both kinds of peracetic acid, irrespective of the content of hydrogen peroxide. After each stage, the pulp was washed in accordance with Example 1. The viscosity after delignification with peracetic acid was 990-1000 dm^3/kg in all tests. The viscosity after bleaching with hydrogen peroxide was 900-920 dm^3/kg in all tests. The results after delignification with peracetic acid and bleaching with hydrogen peroxide, appear from the Table below.

TABLE V

Test No.	Amount of PAA (kg/tonne)	Kind of acid	Brightness after PAA (% ISO)	Brightness after H_2O_2 (% ISO)
1	3.4	PAA-1	45.1	77.9
2	3.4	PAA-2	44.0	77.0
3	11.2	PAA-1	49.9	79.8
4	11.2	PAA-2	48.3	77.9
5	22.4	PAA-1	54.9	81.5
6	22.4	PAA-2	52.7	79.6

It is evident from the Table that treatment of pulp in accordance with the present invention with an equilibrium peracetic acid with a higher content of hydrogen peroxide (PAA-1), has a more positive effect on the brightness after the treatment with peracetic acid as well as the bleaching with hydrogen peroxide, while at the same time the difference in viscosity is very limited.

Claims

1. A process for delignifying and bleaching lignocellulose-containing pulp, characterised in that the pulp is delignified with a peracid or salts thereof, whereupon the pulp is treated with a complexing agent, and subsequently bleached with a chlorine-free bleaching agent comprising at least one of a peroxide-containing compound, ozone or sodium dithionite, or optional sequences or mixtures thereof.

2. A process according to claim 1, characterised in that the lignocellulose-containing pulp is a chemically digested pulp.

3. A process according to claim 1 or 2, characterised in that the peracid is peracetic acid.

4. A process according to claim 3, characterised in that the delignification with peracetic acid is carried out at a pH in the range of from 3 up to 10.

5. A process according to any of the preceding claims, characterised in that the peroxide-containing compound consists of hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.

6. A process according to any of the preceding claims, characterised in that the pulp is washed after the treatment with a complexing agent at a pH of at least about 4.

7 A process according to any of the preceding claims, characterised in that the complexing agent is a nitrogenous organic compound.

8. A process according to claim 7, characterised in that the nitrogenous organic compound is diethylenetriaminepentaacetic acid (DTPA) or ethylenediaminetetraacetic acid (EDTA).

9. A process according to any of the preceding claims, characterised in that the treatment with a complexing agent is carried out at a pH in the range of from about 2.5 up to about 11.

10. A process according to any of the preceding claims, characterised in that the delignification with peracid is preceded by an oxygen stage.

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(54) Title: METHOD OF BLEACHING PULP WITHOUT USING CHLORINE CHEMICALS

(57) Abstract

The present invention relates to a method of treating chemical paper pulp, in which the pulp is first pH-adjusted to a pH of between 1 and 6 and then treated with ozone and a chelating agent with the aim of reducing the kappa number, after which the pulp is washed and immediately thereafter bleached with peroxide, with the chelating agent being added after the ozonisation without any intervening wash.

A - ZQ - P

Method of bl aching pulp without using chlorin chemicals

The environmental protection authorities are placing ever more stringent demands on the pulp industry to decrease the use of chlorine gas in bleaching. Permitted discharges of organic chlorine compounds (AOX) together with the effluent water from the bleaching plant have gradually been lowered and are now at such a low level that pulp mills have in many cases stopped using chlorine gas. Instead, chlorine dioxide is used as the sole bleaching agent. For the same bleaching effect, chlorine dioxide forms lower quantities of AOX than does chlorine gas. However, the use of chlorine dioxide has also been called into question. On the one hand, the environmental protection authorities in certain countries demand that the discharges of organic chlorine compounds should be reduced to such a low level that it is scarcely possible to meet the requirements even when using only chlorine dioxide for bleaching. On the other hand, environmental movements in several countries, especially in Germany, have persuaded consumers to demand paper products which have been bleached entirely without using either chlorine gas or chlorine dioxide.

The pulp industry is therefore searching for methods which permit bleaching of pulp without using these chemicals. One such method has been developed by the Swedish company Eka, which supplies bleaching chemicals to the pulp industry. The bleaching method, which is termed LIGNOX (see SE-A-8902058), involves the unbleached pulp first being delignified with oxygen and then, after washing, being treated with EDTA or another suitable chelating agent in order to remove heavy metals bound within the pulp. After the EDTA stage (Q), there follows an intensive peroxide bleaching stage (P), i.e. hydrogen peroxide. The charge of hydrogen peroxide (H_2O_2) is relatively high, being 15-35 kg per ton of pulp, depending on the required brightness and

on the bleachability of the pulp. The time is quite long, being 4 hours or more, and the temperature high, being 80-90°C.

However, the lignox method only provides a limited increase in brightness. The maximum brightness obtainable depends on the bleachability of the pulp and on the charge of peroxide. Brightnesses in the range of from 80-82 ISO have been recorded. Further bleaching stages over and above the peroxide stage are required in order to achieve higher degrees of brightness.

In this connection, ozone is a bleaching chemical of interest. Several experiments have shown that the use of an ozone bleaching stage (Z) results in the lignin content being decreased, i.e. in the kappa number being reduced. This is important, since a pulp bleached only with peroxide or oxygen/peroxide still contains a relatively high content of lignin, which affects the colour reversion tendencies of the pulp. On being heated or irradiated with sunlight, the pulp yellows. Further lignin is removed by ozone treatment, resulting in the brightness of the pulp becoming more stable.

Eka has shown that oxygen-bleached sulphate pulp which has been treated with EDTA in order to remove heavy metals and subsequently bleached with peroxide and ozone, in accordance with the sequence QPZ, yields brightnesses in the range from 82-87 ISO, depending on pulp type. By extending the bleaching sequence with an additional peroxide stage, and bleaching in accordance with the sequence QPZP, brightnesses in the range from 87-89 ISO can be achieved, depending on pulp type, see "Non Chlorine Bleaching", J. Basta, L. Andersson, W. Hermansson; Proceedings March 2-5, 1992 - Westin Resort - Hilton Head - South Carolina; Copyright by Miller Freeman Inc.

In another patent application, SE9101300 (SE-B-468355), Eka has described an additional bleaching method in which chelating agents are used prior to an ozone or peroxide stage. This application principally

relates to ozone being used directly after a chelating-agent stage.

A prerequisite for achieving high degrees of brightness while consuming only moderate quantities of bleaching agent is that the pulp, prior to bleaching, should have been delignified to a low kappa number, preferably to a kappa number lower than 16. Normally, there is a deterioration in quality, above all a loss of fibre strength, if delignification in the digester house, and oxygen delignification, are taken too far. Nevertheless, in order to achieve a brightness of from 85-90% ISO, as required by the market, and acceptable strength, it is a prerequisite, in order to be able to carry out a chlorine-free bleaching process, that the pulp be produced by a disclosure process which yields a low kappa number, less than 20 and preferably less than 15, and a viscosity of at least about 1000 dm^3/kg. This process should preferably contain an oxygen-delignification stage. However, using the modified cooking methods which have been developed in recent years, it has proved possible to achieve very low kappa numbers without any loss of strength. For example, it is possible, using a modification of Kamyr's continuous cooking process MCC (modified continuous cooking) combined with MC-oxygen-delignification, to get down to, and even below, kappa numbers of 10 for soft wood and 8 for hard wood, with strength properties being retained; if use is additionally made of Kamyr's patented ITC (IsoThermal Cooking) process, even lower kappa numbers can be obtained, with kappa numbers of less than 15 after the digester easily being achieved, which, in the case of soft wood, provides kappa numbers of less than 10 after oxygen delignification.

The modification in accordance with the ITC or MCC process involves the Hi-heat washing zone in the lower part of the continuous digester also being utilized for countercurrent cooking (see EP-A-476230). This is brought about by heating to full cooking temperature in the Hi-heat circulation and by adding

alkaline cooking liquid to this same circulation. The total cooking time in countercurrent is thereby extended to 3-4 hours as against about 1 hour in the case of conventional MCC. This results in a very low concentration of lignin being obtained at the end of the cooking, in turn providing improved selectivity in the delignification, i.e. the lignin in the wood is released efficiently without the cellulose being attacked to any appreciable extent. By these means, the cooking and oxygen delignification can be carried out down to very low kappa numbers without impairing the properties of the pulp, thereby ensuring that bleaching with chemicals of the peroxide, etc., type can be used for bleaching up to full brightness with the properties of the pulp at the same time remaining acceptable.

As is evident from the publications cited above, known technique indicates that a Q stage, i.e. a chelating agent, should always be used prior to a Z or a P stage, preferably with an intermediate wash.

The object of the present invention is to bring about a method of bleaching pulp without using chlorine-containing agents, with the use of ozone and peroxide, these latter chemicals being used as efficiently as possible with a view to achieving a finally bleached pulp having a brightness as required by the market.

Somewhat surprisingly, in experiments carried out at Kamyr, it has been possible to establish, contrary to that which has been indicated above, that improved bleaching results are obtained if no chelating agent is used when the bleaching sequence is initiated with an ozone stage. Over and above this, it has also been possible to establish, thereby further reinforcing the surprising effect, that when, in conformity with the invention, the ozone stage is followed by a peroxide stage, it is better not to carry out a wash aft r the ozone stage before adding the chelating agent. Thus, a very good effect has been observed at Kamyr when an ozonization is initially carried out

(without adding chelating agent), and this is then succeeded directly by the addition of chelating agent, after which there follows a wash before bleaching is carried out using peroxide.

In addition to this, it has been found, altogether surprisingly, that it is of great importance when the pH adjustment is carried out in relation to the addition of chelating agent. In this connection, it has been found to be completely inappropriate to make the pH adjustment before adding chelating agent. By far the best result is obtained when the chelating agent and alkali are added simultaneously. Good results are also obtained when the alkali charge is added after adding the chelating agent. It is most preferable for the simultaneous addition to be carried out in a mixer.

It has been possible to establish that perfectly satisfactory brightness, i.e. reaching 85-90% ISO, can be obtained when the pulp is bleached in an acid (pH adjusted to the region of from 2-6, preferably to about 3) stage with ozone, after which the pulp is treated directly with chelating agent, and is pH-adjusted (addition of alkali), without any preceding wash. The pH adjustment can be carried out prior to, at the same time as, or after, the addition of the chelating agent. The pulp is subsequently washed in at least one stage, where appropriate several stages, so that a very good degree of washing efficiency (at least 80%, preferably 90%, and even more preferably greater than 95%) is achieved. This procedure results in a significantly improved reduction in substances, such as, for example, principally manganese, which are harmful for the subsequent peroxide bleaching. After the wash, the pH of the pulp is adjusted to that level which is most favourable for the subsequent peroxide bleaching. The pH is then within the range of from 8-13, most frequently of from 10-12. In connection with the abovementioned treatment, the pulp can also be treated with an alkaline earth metal, such as, for example, Mg or Ca (salts thereof). The peroxide is

added directly after this treatment. The pulp is washed after the peroxide treatment.

The method according to the invention results in the peroxide stage having a significantly improv d effect as compared with previously known methods (Lignox, QPZ, QPZP, etc.).

EXAMPLE 1

Experiments were carried out on oxygen-delignified sulphate pulp of soft wood which was washed. The pulp had a kappa number of 15.7 and a viscosity of 990 dm^3/kg. The pulp contained 48 g/BDMT Mn. Some of the pulp was treated in accordance with a previously known procedure using chelating agent prior to the ozone stage, and some in accordance with the invention, where chelating agent was added directly after the acid ozone stage. After that, the pulp was peroxide-bleached in a similar manner in both cases. Q indicates treatment with chelating agent. Method 1 describes a known procedure, method 2 describes the procedure according to the invention.

EXPERIMENTS

Original pulp

	Method 1	Method 2
Kappa number	15.7	15.7
Viscosity, dm^3/kg	990	990
Loss on washing kgCOD/-BDMT	5	5
Mg g/BDMT	356	356
Mn g/BDMT	48	48

Stage 1

Pretreatment

Consistency %	10	10
Temp.°C	50	50
Time, min.	60	60
pH	5.8	4.5
Charge of EDTA kg/BDMT	2	0

Ozonization

Consistency %	10	10
pH	3	3
Charge of H_2SO_4 kg/BDMT	5	5
Charge of O_3 kg/BDMT	6	6
Temp.°C		

After-treatment

Consistency %	10	10
Temp. °C	50	50
Time, min.	25	25
Charge of NaOH kg/BDMT	15	7
Charge of EDTA kg/BDMT	0	2

Pulp after stage 1

Kappa number	8.2	8.2
Viscosity dm^3/kg	813	802
Mg g/BDMT	152	101
Mn g/BDMT	24	0.6

Stage 2

Peroxide treatment		
Consistency	10	10
Temp. °C	85	85
Charge of $MgSO_4$ kg/BDMT	3	3
Time, min.	240	240
Charge of H_2O_2 kg/BDMT	35	35
Final pH	10.9	10.7

Pulp after stage 2

Kappa number	4.2	2.7
Brightness % ISO	71	85
Viscosity	695	703

EXAMPLE 2

Oxygen-bleached soft wood pulp was acidified to pH 3. After that, it was divided into three parts. EDTA was added first to part one, followed by NaOH 10 minutes later. Both chemicals were added simultaneously to part two, and NaOH was added first to part three, followed by EDTA 10 minutes later. After the treatment, the pulps were washed. The pulp consistency was about 10%.

Results

	Contents (ppm)			
	Mg	Mn	Cu	Fe
Original pulp	290	47	1.4	21
Alt.1 (Q NaOH)	178	3.2	0.81	15
Alt.2 (Q + NaOH)	104	0.69	0.49	11
Alt.3 (NaOH Q)	214	22	1.1	16

The results demonstrate that substantially improved results can be achieved in the chlorine-free bleaching which has been described when use is made of

the invention. The substantially lower content of Mn on entry to the P treatment, as elicited by the invention, provides a drastically improved brightness combined with good viscosity.

It will be evident to the person skilled in the art that the described procedure for peroxide bleaching can be carried out in a number of different ways, and under different conditions, and that this merely constitutes one example. (Time, temp., charge of H_2O_2, pH, pulp consis., etc., can be varied.) It will be evident, too, that O_2 can be used in conjunction with the peroxide treatment.

Patent claims

1. Method of treating chemical paper pulp, in which the pulp is first pH-adjusted to a pH of between 1 and 6 and then treated with ozone and a chelating agent with the aim of reducing the kappa number, after which the pulp is washed and immediately thereafter bleached with peroxide, c h a r a c t e r i z e d i n that the chelating agent is added after the ozonization without any intervening wash, and that the pulp is pH-adjusted by adding alkali together with or after the addition of chelating agent, to a pH exceeding 3.

2. Method of treating chemical paper pulp according to Patent Claim 1, c h a r a c t e r i z e d i n that the pulp is pH-adjusted by adding alkali, to a pH exceeding 4 and more preferably between 4 and 6.

3. Method of treating chemical paper pulp according to Patent Claim 1, c h a r a c t e r i z e d i n that the reduction of the kappa number in the ozone stage exceeds 20%, preferably 30% and more preferably 40%.

4. Method of treating chemical paper pulp according to Patent Claim 1, c h a r a c t e r i z e d i n that the charge of peroxide exceeds 5 kg/BDMT, preferably 8 kg/BDMT.

5. Method of treating chemical paper pulp according to Patent Claim 1, c ha r a c t e r i z e d i n that the temperature in conjunction with the ozonization is between 20 and 70 C, preferably 30 and 50 C.

6. Method of treating chemical paper pulp according to Patent Claim 1, c h a r a c t e r i z e d i n that the concentration of the pulp is between 5

and 25%, preferably 7 and 20% and most preferred between 7 and 17 %.

7. Method of treating chemical paper pulp according to Patent Claim 1, characterized in that the ozonization takes place at a pH of from 1-6, preferably at a pH of from 2-4 and more preferably at a pH of about 3.

8. Method of treating chemical paper pulp according to Patent Claim 1, characterized in that the content of manganese in the pulp on entry to the peroxide stage is less than 5 g/BDMT of pulp, preferably 1 g/BDMT of pulp and more preferably 0.5 g/BDMT.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 94/00462

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/10, D21C 9/16, D21C 9/153
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO, A1, 9314262 (SUNDS DEFIBRATOR INDUSTRIES AKTIEBOLAG), 22 July 1993 (22.07.93), page 5, claim 1 --	1-4,6-7
A	US, A, 4450044 (BJØRN H. FRITZVOLD ET AL), 22 May 1984 (22.05.84), column 2, line 54 - column 3, line 26 --	1-8
A	EP, A1, 0426652 (LENZING AKTIENGESELLSCHAFT), 8 May 1991 (08.05.91), page 11, line 25 - line 59 -- --------	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion f the international search	Date of mailing of the international search report
20 Sept 1994	23 -09- 1994
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INTERNATIONAL SEARCH REPORT
Information on patent family members

27/08/94

International application No.
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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO-A1-	9314262	22/07/93	AU-A-	3412593	03/08/93
			CA-A-	2124088	22/07/93
			SE-B-	469842	27/09/93
			SE-A-	9200152	22/07/93
US-A-	4450044	22/05/84	CA-A-	1119360	09/03/82
			SE-B,C-	439508	17/06/85
			SE-A-	7902901	05/10/79
EP-A1-	0426652	08/05/91	SE-T3-	0426652	
			AU-B-	636173	22/04/93
			AU-A-	6455290	02/05/91
			CA-A-	2028788	01/05/91
			DE-D-	59005677	00/00/00
			JP-A-	3152286	28/06/91
			TR-A-	24891	01/07/92